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Anomalous High Photocurrents in Nanostructured Electrodes: a new local microchip power source

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Anomalous High Photocurrents in Nanostructured Electrodes: a new local microchip power source

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Abstract follows

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Abstract

An increase in photocurrent has been observed at silicon electrodes coated with nanostructured porous silica films as compared to bare, unmodified silicon. Ultimately, to utilize this effect in devices such as sensors or microchip power supplies, the physical phenomena behind this observation need to be well characterized. To this end, Electrochemical Impedance Spectroscopy (EIS) was used to characterize the effect of surfactant-templated mesoporous silica films deposited onto silicon electrodes on the electrical properties of the electrode space-charge region in an aqueous electrolyte solution, as the electrical properties of this space-charge region are responsible for the photobehavior of semiconductor devices. A significant shift in apparent flat-band potential was observed for electrodes modified with the silica film when compared to bare electrodes; the reliability of this data is suspect, however, due to contributions from surface states to the overall capacitance of the system. To assist in the interpretation of this EIS data, a series of measurements at Pt electrodes was performed with the hope of decoupling electrode and film contributions from the EIS spectra. Surprisingly, the frequency-dependent impedance data for Pt electrodes coated with a surfactant-templated film was nearly identical to that observed for bare Pt electrodes, indicating that the mesoporous film had little effect on the transport of small electrolyte ions to the electrode surface. Pore-blocking agents (tetraalkylammonium salts) were not observed to inhibit this transport process. However, untemplated (non-porous) silica films dramatically increased film resistance, indicating that our EIS data for the Pt electrodes is reliable. Overall, our preliminary conclusion is that a shift in electrical properties in the space-charge region induced by the presence of a porous silica film is responsible for the increase in observed photocurrent.

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Introduction

In an on-going collaboration with the laboratory of Vitaly Vodyanoy at Auburn University, surfactant-templated silica films on silicon electrodes have been investigated for use as supports in novel lipid bilayer/ion channel membrane-based biosensors (the purpose of the water-containing porous film being to serve as an ionic reservoir, facilitating measurement of ion gating events across the lipid membrane). Several interesting phenomena have been observed in electrical measurements of these silicon/mesoporous silica/lipid bilayer constructs. First, the magnitude of the current change between the open and closed states of the ion channels for mesoporous silica supported membranes was found to be over ten times greater than that seen for membranes at bare silicon. Also, the current-voltage characteristics of these supported membranes were significantly different than for membranes at bare silicon. Finally, when illuminated with light, electrodes modified with a mesoporous film exhibited a sharp current transient followed by a quasi-steady state current that were both ca. 100x those observed at a bare silicon electrode (**Figure 1**). It was hypothesized that these effects could be a result of changes in the electronic properties of the semiconductor near-surface region (the space charge layer) induced by the presence of the charged silica film. This report summarizes our efforts to characterize the electronic properties of the semiconductor surface with and without a mesoporous film, and also the ionic transport properties of the mesoporous film itself, using electrochemical impedance techniques.

Mesoporous Support

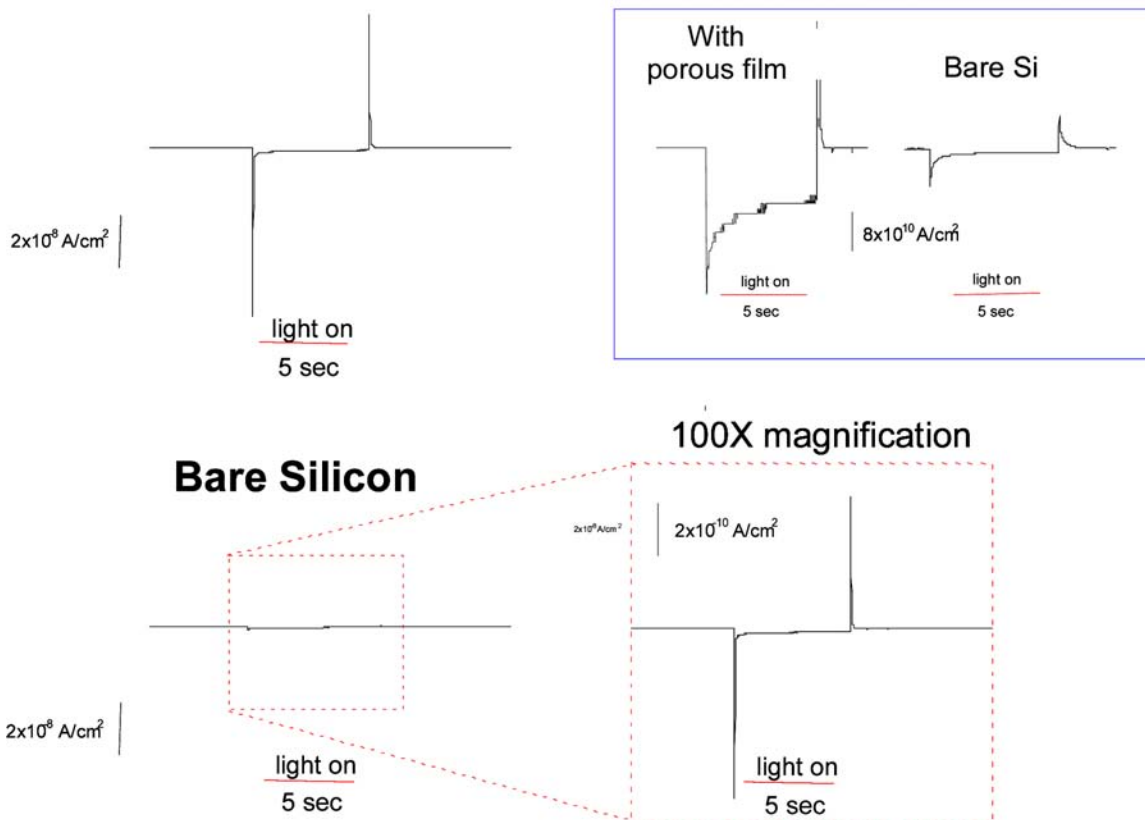


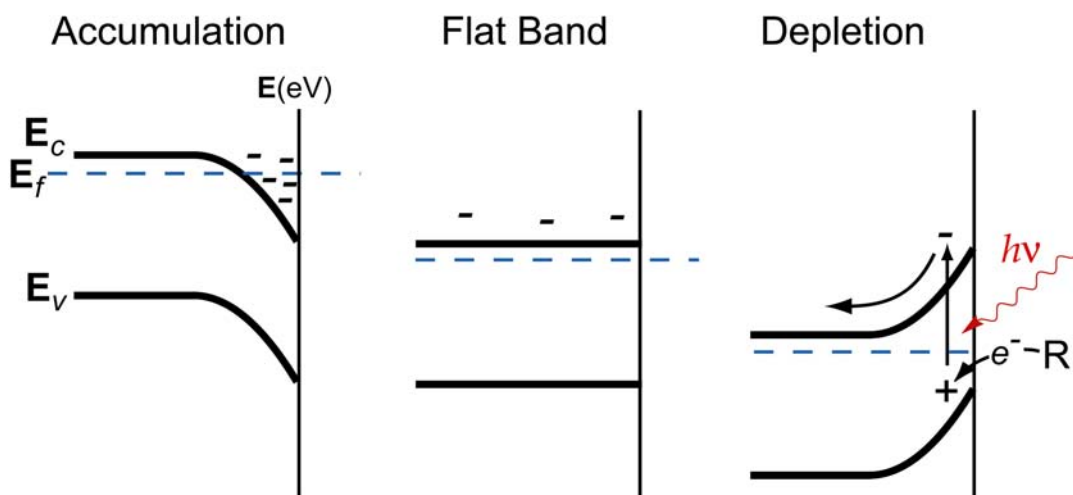
Figure 1. Transient and quasi-steady state photocurrents measured for a silicon electrode prepared with or without a mesoporous silica film.

Background

Figure 2a illustrates the band diagram of a moderately doped n -type semiconductor electrode at the semiconductor/solution interface [1]. E_c and E_v are the conduction and valence bands of the semiconductor material, while E_f is the Fermi level, defined as the average energy of electrons in the system (for n -doped semiconductors, this level lies just below the conduction band). *Band bending* occurs between the field-free interior of the semiconductor and the semiconductor/electrolyte junction: under ideal conditions, the energies of E_c and E_v are pinned at this interface as most of the potential drop in the system occurs in the layer of band bending, called the *space charge region*. The degree and direction of band bending depends on the applied potential and the buildup of induced charge in the space-charge region. As the potential is scanned negative, the band energies are bent downward, and electrons (the majority carriers in n -doped materials) are concentrated near the interface. In this condition (known as *accumulation*) the electrode is capable of reducing (donating electrons to) solution species, but oxidations are not possible due to the lack of holes (the *minority carrier*) in the space charge region. At positive potentials, the bands are bent upwards, and the concentration of electrons at the surface is decreased, a state known as *depletion*. In depletion, adsorption of light with energies greater than the band gap can promote an electron from the valence band to the conduction band, creating a hole in the space charge region, which can then accept an electron from a solution species (oxidation). The resulting electrical signal is the photocurrent. Although capable of oxidation while in depletion, reductions (the donation of electrons to solution species) are not possible at n -doped semiconductor electrodes in this potential range.

Intermediate between these two cases is the *flat-band potential*, E_{fb} . Here, both E_c and E_v are unbent in the space charge region of the semiconductor. Because E_{fb} is a function of parameters such as doping level or excess surface charge, measurement of this potential can yield important insights into the electronic structure of the semiconductor. The flat band potential is typically measured by plotting $1/C_{sc}^2$ vs. E , the

A



B

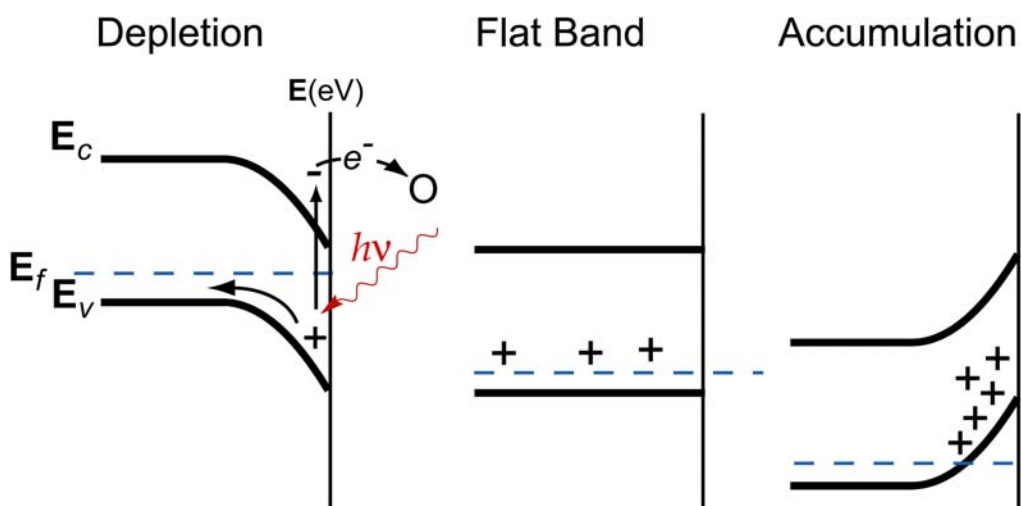


Figure 2. a) Band diagram for an *n*-type semiconductor, and b) band diagram for a *p*-type semiconductor.

applied potential. C_{SC} (the capacitance of the space charge region) is obtained from AC impedance measurements of the electrode under depletion conditions. Ideally, this plot will be linear, and extrapolation to the potential axis will give E_{fb} . However, the presence of surface states at the semiconductor/electrolyte interface can impair this analysis. For silicon electrodes, such states are associated with charge trapping between the silicon and the ubiquitous SiO_2 layer. For *n*-type silicon, this problem can be exacerbated by growth of SiO_2 under depletion conditions by photogeneration of holes at the silicon surface. Addition of either F^- or an electron donor to the electrolyte solution can circumvent this problem to some extent, but modification of the Si surface with a silica film prevents the former and complicates the latter due to charge interactions between the added redox couple and the pore walls.

Because excess surface charge at the semiconductor/electrolyte interface can readily affect the charge distribution inside the space charge region, the degree of band bending (and thus the flat band potential) is sensitive to the presence of an ionic film deposited onto the electrode surface. For example, a negatively charged silica film will increase the number of positive carriers (holes) in the space charge region, shifting the flat band potential to less negative potentials. Conversely, a positively charged film will increase the concentration of electrons near the surface of the semiconductor, moving the flat band potential negative with respect to the system reference (such as a Ag/AgCl electrode).

The properties of *p*-doped semiconductors are reversed with respect to *n*-doped materials (**Figure 2b**). Although the potential-dependent direction of band bending remains the same as for the case of *n*-doped materials, accumulation occurs at potentials *positive* of E_{fb} , while depletion conditions are found at potentials *negative* of E_{fb} . In depletion, a *p*-doped semiconductor acts as a photocathode, donating electrons to solution species (reduction). Under conditions of accumulation, only oxidations are possible.

Using these fundamental properties of semiconductor electrodes, a plausible mechanism for the increase in observed photocurrent upon modification of the silicon surface with a mesoporous silica film can be deduced. **Figure 3** is a current-voltage curve for an *n*-doped semiconductor electrode under illumination. Positive of the flat band potential, there is an anodic photocurrent. Because addition of a negatively charged

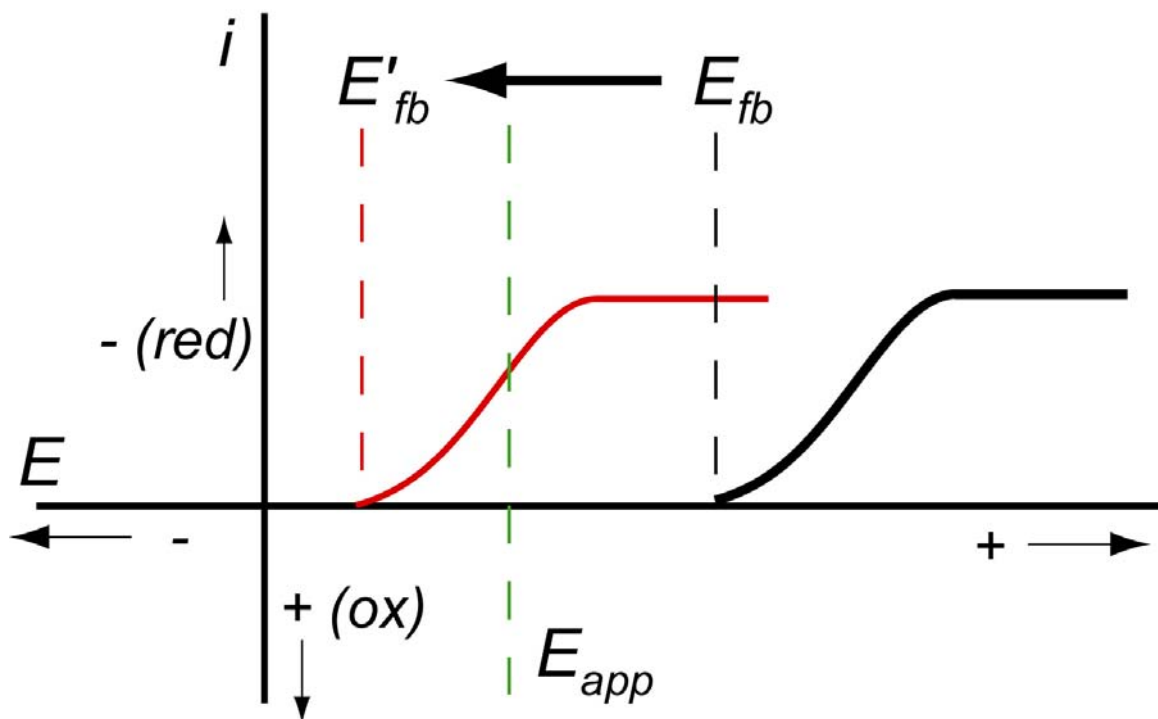


Figure 3. Current-voltage curve for an n -type semiconductor under illumination, illustrating the proposed hypothesis for the mechanism of increased photocurrent after modification of n -doped silicon electrodes with a mesoporous silicate film.

silica film induces an increase in positively charged carriers (holes) in the space charge region, the flat band potential is shifted from E_{fb} to E'_{fb} . If the photocurrent is observed at a fixed potential (E_{app}) negative of E_{fb} but positive of E'_{fb} then a dramatic rise in anodic current will be observed. (Alternatively, E_{app} could be slightly positive of E_{fb} and the same effect would be seen, although to not as great of an extent). To verify this hypothesis, we attempted to measure the flat band potential of both bare and mesoporous silica-modified silicon electrodes using Electrochemical Impedance Spectroscopy (EIS).

It should be noted that shifts in electronic band structure in the space charge region have previously been reported for *n*-type silicon electrodes modified with surfactant-templated silica films incorporated into a metal-insulator-semiconductor (MIS) device for gas sensing applications [2]. Under AC photo illumination, differences in surface voltage between silicon electrodes modified with either cubic or hexagonal silica films were measured. However, these differences were explained in terms of gas accessibility and not inherent effects of the film on the electronic band structure.

Results and Discussion

To measure the effect of mesoporous silicate films on the flat band potential of silicon electrodes, surfactant-templated Al-doped silica films were deposited onto *p*-doped Si substrates (experimental details are given below). *p*-doped electrodes were selected for use in initial studies because of their greater stability under depletion conditions when compared to *n*-doped materials. Experimentally, instead of shifting E_{fb} potential to more negative values when modified with a negatively charged silica layer (as with *n*-doped silicon electrodes), E_{fb} should move to more positive values. Al-doping substantially increases the hydrolytic stability of the silica layer [3]. Experiments were conducted in 50 mM PBS buffer under dark conditions, and referenced to an Ag/AgCl electrode.

Figure 4 shows $1/C_F^2$ plotted as a function of potential for a bare *p*-doped silicon electrode and a *p*-doped silicon electrode overcoated with a Brij 56-templated film (ca. 3 nm pores), with data at both 500 Hz and 10,000 Hz. To calculate C_F , an assumption was made that space charge capacitance dominates the impedance characteristics of the

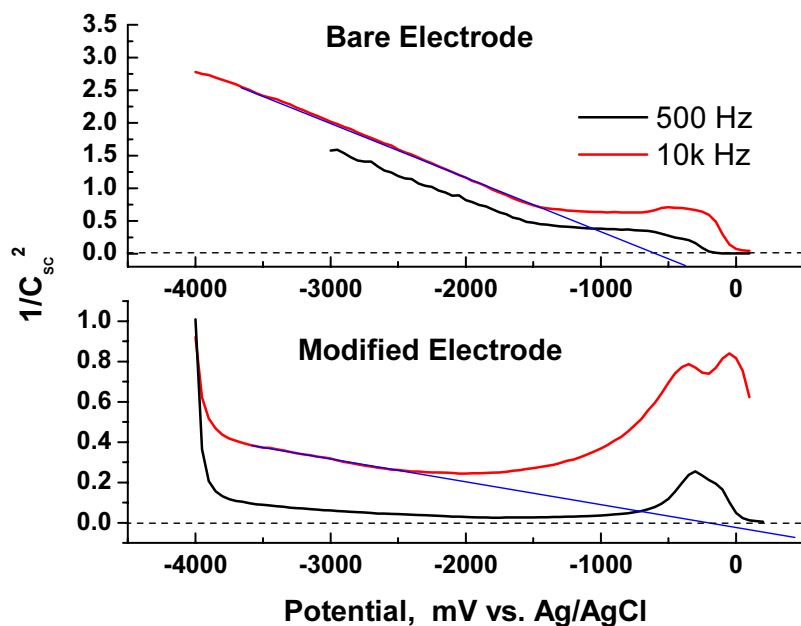


Figure 4. $1/C^2$ vs. potential for bare and mesoporous-film modified *p*-type silicon electrodes. Capacitance is in F/cm^2 . The blue line represents the extrapolation to $1/C^2 = 0$.

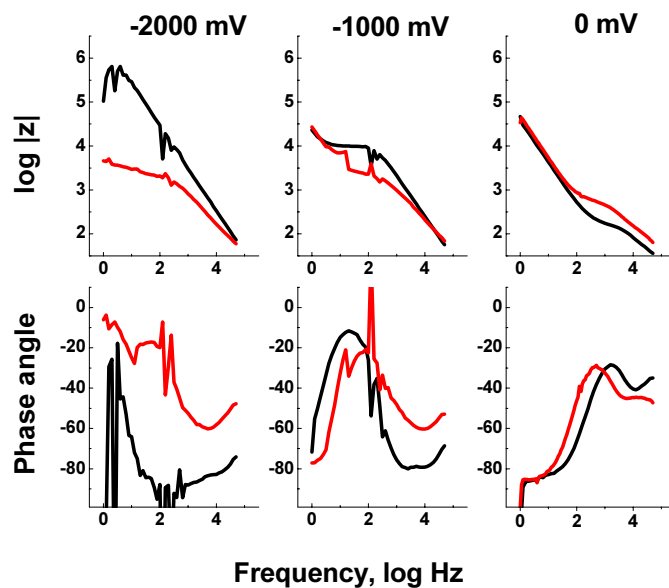


Figure 5. Impedance spectra for bare (black line) and mesoporous silicate film modified (red line) *p*-doped silicon electrodes.

system, making the equivalent circuit a simple series capacitor. Above ca. -2.0 V the capacitance is clearly dominated by surface states, while electrical breakdown of the electrode occurs at about -4.0 V (at least for the data from electrodes modified with mesoporous silicate films). Between these extremes, this data is linear, as would be expected for semiconductor materials under depletion conditions. Extrapolation of this linear regime to $1/C_F^2 = 0$ yields a flat band potential of about -0.58 V for the unmodified electrode, and -0.14 for the electrode coated with the mesoporous silicate film. If accurate, these numbers would be consistent with the present hypothesis. However, these numbers are suspect for two reasons. First, the flat band potential is different at the two measured frequencies. Although the capacitance contribution from surface states decreases with an increase in measurement frequency, even at 10k Hz surface states still appear to dominate the data in **Figure 4**. Second, to accurately measure E_{fb} from extrapolation of the $1/C_F^2$ vs. V data, it would be desirable to measure points exclusively from space charge capacitance near this potential. Nonetheless, even with these complications, the data in **Figure 4** clearly show a change in electronic properties of the silicon electrode after modification with a mesoporous silicate film.

To attempt a better understanding of the impedance characteristics of the modified silicon electrodes utilized in the above study, frequency-dependent impedance spectra were measured at several potentials of interest (**Figure 5**). It was hoped that a particular frequency and potential region could be identified where the electrical properties of the space charge layer inside the electrode could be isolated from all other contributions. However, the data was not found to be easy to interpret. At high frequencies, solution resistance should dominate the impedance spectrum. Unfortunately, there is no plateau in the impedance data in **Figure 5**, even at 50 kHz. Also, the phase angle at high frequency, which should be 0° for a pure solution resistance, clearly has significant capacitive character (a pure capacitance giving a phase angle of -90°). As the frequency is increased, it would be expected that the observed surface state capacitance would decrease. There are no features in either the phase angle or impedance data that can be definitely attributed to surface states, however. One unknown in the analysis of this data is the effect of the mesoporous film on ionic transport to the silicon surface. Hypothesizing that some of the difficulty in data interpretation was due to the effect of

this film, it was decided that an impedance study of surfactant-templated silicate films at *platinum* electrodes would assist in understanding the spectra at silicon electrodes. By utilizing platinum as the electrode for these studies, the effect of the space charge region and surface states would be removed, isolating the characteristics of the modifying film (and double layer capacitance at the platinum electrode, a well-characterized phenomenon).

Representative data from this study is shown in **Figure 6**. Films templated with different pore sizes were tested (from less than 2 nm to ca. 6-7 nm), as well as the effect of pore structure (2D hexagonal vs. cubic mesophase), ionic strength, and the presence of known pore blockers (tetraalkylammonium salts). For all films, however, both the impedance and phase angle behavior was nearly identical to that of a bare platinum electrode, demonstrating that the films tested had no effect on ionic transport under the conditions studied. A non-templated silica film was also investigated. In this case, ionic transport was completely blocked, as indicated by the high impedance and capacitance (from film charging) shown in **Figure 6**.

In conclusion, the electronic characteristics of silicon electrodes were shown to be sensitive to modification of the electrode surface with a mesoporous silicate film. The measured flat band potentials, although suspect due to surface state capacitance, were found to be consistent with the starting hypothesis that increased photocurrents at silicon electrodes at constant potential are due to shifts in E_{fb} induced by the presence of a porous silicate film. A definitive conclusion will require further studies, however. Finally, surfactant-templated silicate films with pore sizes from < 2 nm to > 6 nm were found to have no effect on ionic transport to the electrode surface under the conditions studied here.

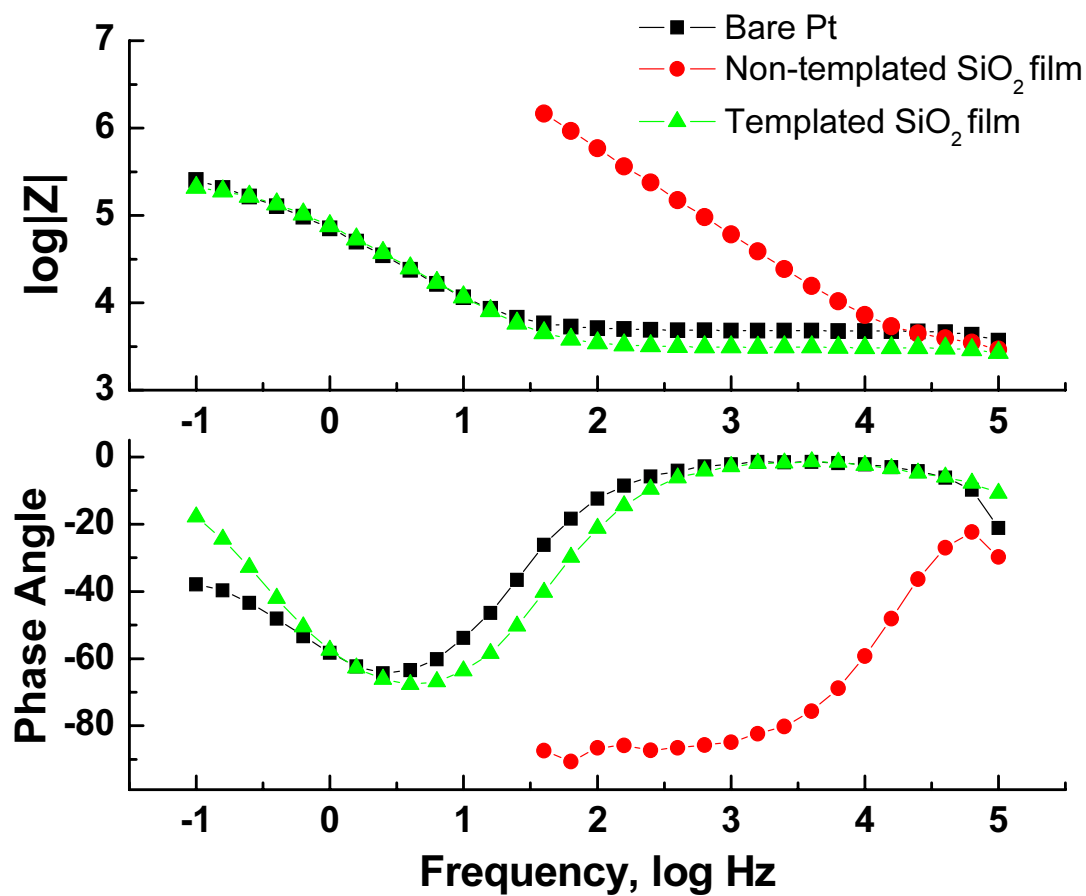


Figure 6. Impedance spectra for bare, surfactant-templated silicate film modified, and non-templated silicate film modified platinum electrodes.

Future Directions

The presence of a thin oxide film at the silicon surface greatly increases the difficulty of data interpretation for both frequency and potential dependent data. For this reason, the use of a semiconductor electrode with greater stability would facilitate these experiments. An example of a suitable electrode material is TiO_2 . Not only is this semiconductor much more stable than silicon, facilitating the measurement of the flat band potential under reasonable conditions, but it is also a technologically important material for applications such as solar energy generation or hydrogen production.

Because of the uncertainty in the interpretation of the impedance data, optical techniques may provide a more direct route for the determination of the flat band potential [4]. In photopotential measurements, the open circuit potential is recorded as a function of illumination intensity: the limiting potential is E_{fb} . Alternatively, the potential-dependent photocurrent (at constant light intensity) can be used to determine E_{fb} .

Impedance measurements should prove useful in characterizing other, more complex mesoporous silicate materials. For example, surfactant-templated films with integral amine functionality have been synthesized which exhibit ion channel-like behavior [5]. Other systems of interest include photoresponsive materials [6] and nanostructured silica/hydrogel composites [7].

Experimental

Impedance measurements were performed with a Voltalab 40 electrochemical interface (Radiometer Analytical) using a 10 mV sine wave of appropriate frequency superimposed on the desired potential. All measurements were made using a Ag/AgCl reference electrode (made in-lab) and a platinum wire counter electrode (surface area calculated to be ca. 10 cm^2). For experiments with silicon electrodes, the measurement area was 0.94 cm^2 , while for experiments with platinum electrodes, the measurements area was 0.02 cm^2 .

Silicon electrode material (0.6 mm thick) was obtained from Silicon Valley Microelectronics. Phosphorous-doped silicon (*n*-type) had a resistivity of 1-10 Ω -cm, while boron-doped silicon (*p*-type) had a resistivity of 6.40-8.60 Ω -cm. An ohmic contact of 500 Å chromium and 2000 Å gold was vapor deposited onto the unpolished backside. Platinum electrodes consisted of platinum-coated Si substrates: electrical contact was made through the platinum coating outside of the o-ring that defined the working area of the electrode.

Film synthesis for Brij 56 (ca. 3 nm pore) and P123 (> 6 nm pore) templated films was as previously reported [3] using a Al/Si ratio of 1:50. The films deposited onto silicon electrodes used Brij 56 in a SiO₂/surfactant mass ratio of 1.06, a ratio used for making films with 3D cubic pore structures. Both Brij 56 and P123 were used to template films for deposition onto the platinum electrodes, in a SiO₂/surfactant mass ratio of either 1.06 or 2.12 (the latter value giving films with 2D hexagonal pores oriented parallel to the substrate surface). Cetyltrimethylammonium bromide (CTAB) was also used to template films with ca. 1.8 nm pores for modification of the platinum electrodes using a different sol recipe than that given above. Either 570 or 670 mg of CTAB was added to a solution of 2.76 g tetraethyl orthosilicate, 0.43 ml of DI H₂O, 0.74 ml of 0.07 N HCl, and 35 mg of AlCl₃ (Al/Si ratio of 1:50) in 12.0 g of ethanol. All films were spin coated at 2000 rpm, and calcined to 450° C for three hours. Although no peeling of platinum was observed at this temperature, some blistering of the Cr/Au ohmic contact was seen. However, the electrical contact between this film and the silicon electrode was not compromised, as tested with a conductivity measurement.

All experiments with the silicon electrodes utilized a 50 mM PBS buffer as the electrolyte. Platinum-electrode experiments were performed with 10 mM Tris buffer (pH 7.0), 10 mM citrate buffer (pH 4.0) or 0.01 M HCl, all with 50 mM NaCl added to increase the ionic conductivity of the solution. Experiments were also run at pH 7.0 with 250 mM KCl added instead of the NaCl, or with 10 mM of a tetraalkylammonium salt pore blocker added (with the alkyl group ranging from C₂ to C₈ in length).

References

- 1) A.J. Bard and L.R. Faulkner, "Electrochemical Methods, 2nd Edition", John Wiley & Sons, New York, 2001
- 2) T. Yamada, H.-S. Zhou, H. Uchida, M. Tomita, Y. Ueno, T. Ichino, I. Honma, K. Asai, and T. Katsube, *Adv. Mater.*, **2002**, *14*, 11, 812-815
- 3) D.R. Dunphy, S. Singer, A. W. Cook, B. Smarsly, D.A. Doshi, C.J. Brinker, *Langmuir*, **2003**, *19*, 10403-10408
- 4) A.W. Bott, *Current Separations*, **1998**, *17*, 87-91
- 5) N.G. Liu, R.A. Assink, B. Smarsly, C.J. Brinker, *Chem. Commun.*, **2003**, *10*, 146-1147
- 6) N.G. Liu, Z. Chen, D.R. Dunphy, Y.B. Jiang, R.A. Assink, C.J. Brinker, *Angewandte Chemie*, **2003**, *42*, 1731-1734
- 7) G. Garnweitner, B. smarsly, R.A. Assink, W. Ruland, E. Bond, C.J. Brinker, *J. Amer. Chem. Soc.*, **2003**, *125*, 5626-5627

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